SATURATED HYDROCARBON POLYMERIC BINDER FOR

ADVANCED SOLID PROPELLANT AND HYBRID SOLID GRAIN


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NOTE:   MINOR JPL CORRECTIONS TO PAGES 1,7,11,12,13,14,16 and 18
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# I.  OBJECTIVE

Union Carbide Corporation, Plastics Division has agreed to provide, on a level of effort basis, between 100.8 and 106.8 direct man months of effort to assist the Jet Propulsion Laboratory in the development of a new or improved polymeric binder for advanced solid propellant and hybrid solid grains.  The detailed objectives are described in Quarterly Report No. 1.

# II.  SUMMARY

A small, continuous, high pressure tube reactor was used to carry out a series of ethylene-neohexene copolymerizations using DMAB as the initiator.  These experiments demonstrated that even in the short residence times which exist in the tube reactor (1-2 minutes), radicals from DMAB disproportionate extensively to yield the hydrogen transfer agent methyl isobutyrate.  This compound is believed responsible for the monofunctionality of the prepolymer made in batch and continuous reactors using DMAB.

A very promising route to a prepolymer of higher functionality than attainable with DMAB or AIBN initiation is being examined.  This involves the telomerization of ethylene/neohexene with $CCl_4$, which places a Cl group on one end of the molecule and $CCl_3$ groups on the other end. Chemical modification of these telomers is in progress, with the goal the conversion of all terminal groups to COOH.

Another reaction sequence for increasing functionality involves the use of organic disulfides as chain transfer agents.  In order to apply this concept to ethylene-neohexene copolymerization we have synthesized three symmetrical disulfide compounds which contain ester functionality.  They are, dimethyl $\tau, \tau'$-dithiodibutyrate, di-t-butyl $\alpha, \alpha'$-dithio bis [isobutyrate] , and dimethyl dithioglycolate.  Ethylene-neohexene copolymerization studies in the presence of these telomerizing agents are in progress.

During the next quarter telomerization studies with $CCl_4$ and the disulfides will be continued.  As soon as possible the most promising of these approaches will be selected for intensive study.

## III.  SCOPE OF PROJECT

The scope of this work has not changed from the program outlined in the work statement.  The experimental program is directed toward improving the functionality of the prepolymer.  The available batch autoclaves have been supplemented by a small, continuous reactor which is now in use.

## IV.  INTRODUCTION

In our fourth quarterly report various factors which might adversely influence the attainment of satisfactory carboxyl functionality levels were examined critically.  The comonomer, neohexene, was analyzed thoroughly for the possible presence of chain transfer impurities ... none were found.  The titrimetric procedure for determining neutralization equivalent was altered to increase its precision and accuracy.  The procedure for measuring number average molecular weight in polar solvents was found to be more reproducible than in non-polar solvents.  The possibility that polymeric anhydrides were present in the prepolymer as a result of thermal treatment during clean-up was tested using a standard anhydride analysis.  No anhydrides were detected.

Preliminary evidence was presented to support the conclusion that DMAB initiator, on decomposition, yields radicals which disproportionate to some extent to methyl isobutyrate and methyl methacrylate.  The former is an active hydrogen transfer agent.  Its presence in the reaction medium would lower the acid functionality of the resulting prepolymer.

These results suggested two experimental approaches which might avoid this problem.  One involved carrying out the copolymerization under continuous, steady state conditions for short residence times.  This approach is very effective in reactions which are affected adversely by side-reaction products which accumulate with time.  The second approach is more radical in that it involves the use of chain transfer agents such as $CCl_4$ and organic disulfides which do not undergo hydrogen transfer reactions.  These two approaches are considered in the succeeding pages of this report.

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# V.  TECHNICAL DISCUSSION

## A.  Preparation of Ethylene-Neohexene Copolymers in the Continuous Tubular Reactor - DMAB Initiator

Last quarter we reported the results obtained when dimethyl azobisisobutyrate (DMAB) was used as initiator for batch copolymerizations of ethylene and neohexene in the stirred autoclave reactor.  These products had low oxygen functionalities as obtained, and after hydrolysis, yielded materials containing one carboxyl group per molecule.  This was explained on the basis of a hydrogen transfer mechanism involving methyl isobutyrate formed from the disproportionation of initiator radicals.

To determine if a product of higher functionality could be prepared under continuous polymerization conditions, we have studied the copolymerization of ethylene and neohexene in a small tubular reactor employing DMAB as initiator.

In this process, comonomers and initiator are fed under pressure into one end of the tubular reactor, which consists of from one to four steel alloy tubes in series (each is 3/16 in. I.D. x 12 ft. long).  The reactants are brought up to the required polymerization temperature as they pass through a heated section of the reactor.  Polymerization occurs throughout the remainder of the tube and the resulting polymer and unreacted monomers are discharged from the exit end of the reactor to be worked up as required.

Table I summarizes the results obtained in these experiments.

Runs 66, 67, 68, 78, 79 and 80 were all run at constant composition and at a jacket temperature of 151°C; however, the operating pressure was varied.  The highest conversions and molecular weights were obtained at 30,000 psi.  In runs 85 and 86 less DMAB was used.  These runs gave higher molecular weights and lower conversions as we had expected.  Runs 81 and 84-B were identical to the first six runs except they were done at the higher jacket temperatures of 171 and 191°C, respectively.  Higher conversions and molecular weights were obtained in these runs.

The functionalities reported for the products were calculated from the oxygen content and the number average molecular weight, and are equivalent to the number of $O_2$ units per molecule.  With the exception of run 81, the functionalities are similar to the functionalities obtained with DMAB in the

## TABLE I

### NEOHEXENE/ETHYLENE COPOLYMERS PREPARED IN THE TUBULAR REACTOR USING DMAB

| Run No. | 66 | 67 | 68 | 78 | 79 | 80 | 85 | 86 | 81 | 84-B |
|---|---|---|---|---|---|---|---|---|---|---|
| **FEED COMPOSITION** | | | | | | | | | | |
| *Wt. % Neohexene | 71.5 | 71.5 | 71.5 | 71.5 | 71.5 | 71.5 | 72.3 | 72.6 | 71.5 | 71.5 |
| Wt. % Ethylene | 26.4 | 26.4 | 26.4 | 26.4 | 26.4 | 26.4 | 26.7 | 26.8 | 26.4 | 26.4 |
| Wt. % DMAB | 2.06 | 2.06 | 2.06 | 2.06 | 2.06 | 2.06 | 1.04 | 0.55 | 2.058 | 2.058 |
| Total Feed, wgt. | 701 | 601 | 556 | 679 | 579 | 668 | 612.1 | 734.5 | 623.2 | 566.4 |
| **REACTION CONDITIONS** | | | | | | | | | | |
| Jacket Temperature, °C | 151 | 151 | 151 | 151 | 151 | 151 | 151 | 151 | 171 | 191 |
| Pressure, mpsig | | | | | | | | | | |
| Average | 20 | 20 | 20 | 20 | 10 | 30 | 30 | 30 | 30 | 30 |
| Deviation | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 | ±2.5 |
| Operating Time, Hrs. | 0.82 | 1.15 | 0.23 | 0.19 | 0.267 | 0.33 | 0.30 | 0.316 | 0.3 | 0.23 |
| Nominal Hold-Up Time, Min. | 2.53 | 4.15 | 0.91 | 0.61 | 1.001 | 1.08 | 1.06 | 0.935 | 1.04 | 0.910 |
| **PRODUCTIVITY** | | | | | | | | | | |
| Yield, Grams | 61 | 53 | 53 | 60 | 35 | 66 | 57 | 57 | 75 | 69 |
| Conversion, % on M's | 8.92 | 9.01 | 9.74 | 9.02 | 6.18 | 10.09 | 9.4 | 7.8 | 12.3 | 12.7 |
| Production Rate, lbs./cu.ft./hr. | 58.2 | 35.9 | 177.1 | 244 | 102 | 154 | 148 | 140 | 194.9 | 230.6 |
| Production Rate, gm. resin/hr. | 74.7 | 46.1 | 227 | 313 | 132 | 198 | 190 | 180 | 250 | 295.7 |
| **PHYSICAL PROPERTIES** | | | | | | | | | | |
| Molecular Weight | 823 | 819 | 815 | 754 | 566 | 823 | 1243 | 1494 | 900 | 946 |
| Brookfield Vis., cps | 4700[23] | 5400[22] | 4500[22] | 3610[23] | 1060[23] | 5200[23] | 28,600 | 49,700 | 7590 | 7350 |
| Sp. Vis., @ 80°C | 0.0303 | 0.0324 | 0.0294 | 0.0297 | 0.0218 | 0.0319 | 0.0503 | 0.0452 | 0.0346 | 0.0273 |
| Wt. % Oxygen | 5.35 | 4.19 | 4.79 | 5.89 | 4.04 | 5.14 | 2.52 | 2.81 | 7.50 | 3.92 |
| Functionality (O) | 1.38 | 1.07 | 1.22 | 1.39 | .72 | 1.32 | 0.98 | 1.31 | 2.11 | 1.16 |
| Description | | | | | | | | | | |
| Remarks | Sl. Hazy, pale yellow | | | | | | | | | |

* Wt. %'s on Total Charge.

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stirred autoclave: not much above one per molecule. In Run 81, however, the functionality was over two O2 per molecule. This particular run was made at a jacket temperature of 171°C and at 30,000 psi pressure.
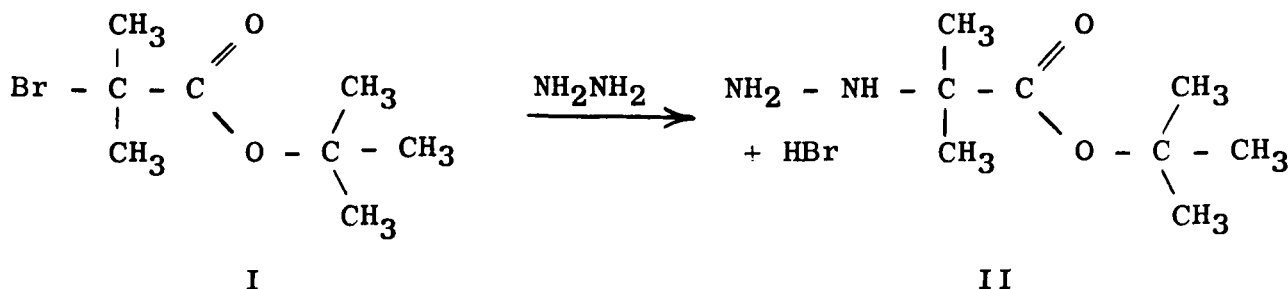
The product from run 81 was then saponified and converted to the -COOH terminated liquid copolymer. An incompatible water soluble fraction was separated from the hydrolyzed product during work up, but was not further characterized. The main product, obtained in 84% yield was analyzed and found to have a number average molecular weight of 877 (in tetrahydrofuran by vapor phase osmometry) and a neutralization equivalent of 902. One infers from these results that on the average there is 0.97 -COOH group per molecule. The elemental oxygen analysis of 4.18 wt. % gives support to this inference, showing the presence of 1.15 $O_2$ units per molecule.

No further work is planned on the products from the other runs because of their low oxygen functionalities.

This study has shown that the tubular reactor is an effective tool for preparing copolymers of ethylene and neohexene in a continuous process. Good control of molecular weight and product comonomer composition has been achieved. However, using DMAB initiator, we have not attained a significant improvement in the functionality of the copolymers from the tubular reactor as compared with copolymer prepared by the batch process in the stirred autoclave. From these results it can be assumed that the radicals from DMAB decomposition disproportionate quite rapidly and extensively to methyl isobutyrate and methyl methacrylate.

## B. Synthesis of DTAB

A key intermediate in the proposed synthesis of the di-tertiary-butyl ester of azobisisobutyric acid (DTAB) is the tertiary-butyl ester of α-bromoisobutyric acid (I).[1] I was prepared in good yield by the route previously outlined. Reaction of I with anhydrous hydrazine gave the monosubstituted hydrazine II as the sole product. No further substitution occurred when II was treated with an excess of I.



I                                                                II

Bromoester I failed to react with aqueous ammonia to give the amino ester III.  III might also have been subsequently

$$I + NH_4OH \longrightarrow NH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - C\underset{O}{\overset{\displaystyle \nearrow O}{\diagdown}} - \underset{\underset{CH_3}{\diagdown}}{\overset{CH_3}{\underset{|}{C}}} - CH_3 \quad + HBr \\ + H_2O$$

$$[o] \diagdown \quad ?$$

DTAB

III

converted to DTAB, via oxidative coupling of the amino groups. No further attempts to synthesize DTAB are planned.
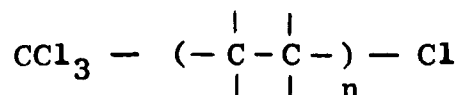
## C. Preparation of Terminally Difunctional Copolymers of Ethylene and Neohexene Using Carbon Tetrachloride as Telogen

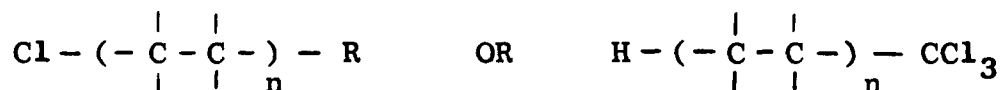The literature contains numerous references[2-6] to the use of carbon tetrachloride as a chain transfer agent, or telogen, in the free radical telomerization of olefins, notably ethylene.  When an olefin is treated with carbon tetrachloride in the presence of a source of free radicals, the following chain reaction is set up:

$$R\cdot \; + \; \underset{/}{\overset{\diagdown}{C}} = \underset{\diagdown}{\overset{/}{C}} \quad \longrightarrow \quad R - \underset{|}{\overset{|}{C}} - \underset{\diagdown}{\overset{/}{C}}\cdot$$

$$R - \underset{|}{\overset{|}{C}} - \underset{\diagdown}{\overset{/}{C}}\cdot \; + \; \underset{/}{\overset{\diagdown}{C}} = \underset{\diagdown}{\overset{/}{C}} \quad \xrightarrow[n \text{ times}]{} \quad R - \left(\overset{|}{\underset{|}{C}} - \overset{/}{\underset{\diagdown}{C}}\right)_n - \overset{|}{\underset{|}{C}} - \overset{/}{\underset{\diagdown}{C}}\cdot$$

$$R - (\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}})_n - \overset{|}{C} - \overset{/}{\underset{\diagdown}{C}}\cdot \; + \; Cl - CCl_3 \quad \longrightarrow \quad R - (\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}})_{n+1} - Cl \; + \; CCl_3\cdot$$

$$CCl_3^{\cdot} \; + \; \underset{/}{\overset{\diagdown}{C}} = \underset{\diagdown}{\overset{/}{C}} \quad \longrightarrow \quad CCl_3 - \overset{|}{\underset{|}{C}} - \overset{/}{\underset{\diagdown}{C}}\cdot$$

$$CCl_3 - \overset{/}{\underset{|}{C}} - C\cdot \; + \; \underset{/}{\overset{\diagdown}{C}} = \underset{\diagdown}{\overset{/}{C}} \quad \longrightarrow \quad CCl_3 - \left(\overset{|}{\underset{|}{C}} - \overset{|}{C}\right)_n - \overset{|}{\underset{|}{C}} - \overset{/}{\underset{\diagdown}{C}}\cdot \qquad \underline{etc.}$$

The net result of this free radical chain reaction is the formation of a large number of molecules containing two

functional groups derived from $CCl_4$:

$$CCl_3 - (-\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} -)_n - Cl$$

And a small number containing one functional group derived from the initiator:

$$Cl - (-\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} -)_n - R \qquad OR \qquad H - (-\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} -)_n - CCl_3$$

The average value of n, called $\overline{DP}n$, the number average degree of polymerization, is given by the following simple expression*:

$$\overline{DP}_n = \frac{[M]}{C \ [S]}$$

where $[M]$ is the concentration of the monomer, $[S]$ is the concentration of telogen, and C is the "chain transfer coefficient." C is the ratio between the rate constant of the chain transfer reaction and the rate constant of the propagation reaction:

$$C \equiv \frac{K_t}{K_p}$$

In the particularly simple case where $K_t = K_p$ and $C \equiv 1$, the $\overline{DP}_n$ is given by the molar ratio of the monomer to telogen, and the relative concentration of the telogen to that of monomer will remain constant.

If $C \neq 1$, the concentration ratio

$$[M] \ / \ [S]$$

will change during the run.

This can be avoided by adding additional material to the reactor to maintain the ratio at some constant value.

Carbon tetrachloride has been used in the telomerization of ethylene to prepare a variety of low molecular weight $\alpha, \alpha, \alpha, \omega$-tetrachloroalkanes, and when $\overline{DP}_n$ is between 2 and 8, these compounds have been converted into a variety of difunctional chemical intermediates[3,4,5]. The chain transfer coefficient for ethylene telomerization by $CCl_4$ is 3.2 for chain lengths of 3 and higher.[6]

---

*See reference 6, Chart 4.

Neohexene has been reacted with $CCl_4$ in the presence of benzoyl peroxide to give a 1:1 adduct. The adduct has the structure:[7]

```
      t-Bu
       \
   H - C - CH2 - CCl3
      /
     Cl
```
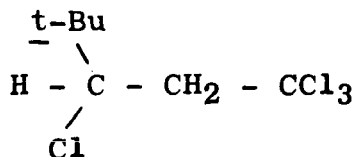
This shows that the bulky $CCl_3\cdot$ radical prefers to add to the less substituted end of the double bond.

No studies of the co-telomerization of ethylene with neohexene have been reported.

We have completed a series of co-telomerization runs using carbon tetrachloride as the telogen in the presence of a small amount of DMAB initiator. These experiments were carried out in the small stirred autoclave. All the reactants were charged at the beginning of the run. The reaction conditions used and the results obtained from these runs are summarized in Table II. The only parameter which was changed during these four runs is the mole ratio of carbon tetrachloride: Monomers.

As we had expected, the $\overline{M}n$ of the resulting telomer was strongly dependent upon the mole ratio of carbon tetrachloride used in the run. An approximate degree of polymerization was calculated from the $\overline{M}n$ for each run, assuming one $CCl_4$ per chain and an average monomer unit weight of 44 (The latter based upon our earlier N.M.R. findings relating the composition of the polymerization mixture to resulting co-polymer composition). Plotting $1/\overline{DP}n$ vs $[S]/[M]$ for each of the four runs, a straight line plot was obtained (See Figure I) having a slope of 8.9. This is the apparent chain transfer coefficient for this particular comonomer charge composition. The actual curve falls off the straight line at low $[S]/[M]$. Whether this represents experimental uncertainty, or a growing importance of chain transfer to DMAB decomposition products, cannot be determined without further experimentation. The latter hypothesis is certainly more consistent with the lower $Cl_2$ functionalities which resulted in runs 90 and 63.

Elemental chlorine and oxygen analyses combined with the number average molecular weight (benzine, V.P.O.) allows us to calculate $Cl_2$ (average of Cl and $CCl_3$) and $O_2$ functionalities. The sum of these functionalities is the number of potentially useful groups per molecule available for chemical transformation. These polymers presumably contain an equal number of Cl and $CCl_3$ groups derived from $CCl_4$ as well as some $-CO_2CH_3$ groups and functionless ends. The latter are derived from carbomethoxy isopropyl radicals and their disproportionation products.
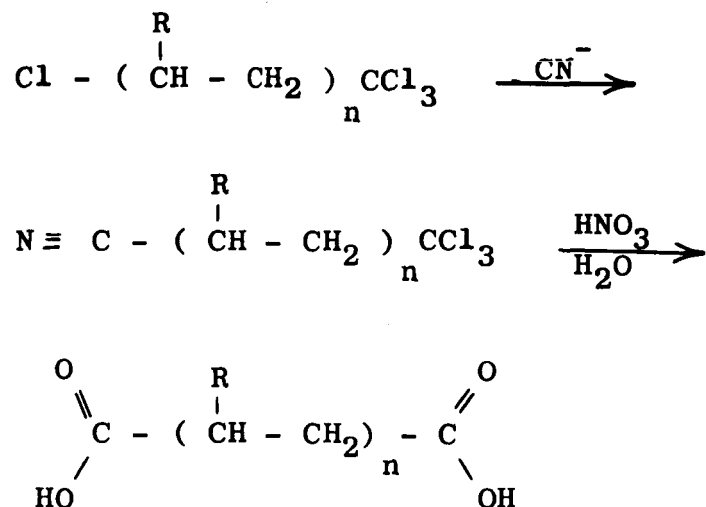
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## TABLE II

### CCl$_4$ TELOMERS OF NEOHEXENE-ETHYLENE

| Run No. 23EMS | 63 | 64 | 65 | 90 |
|---|---|---|---|---|
| **CHARGE:** | | | | |
| Mol Ratio CCl$_4$/Monomers, $^{(S)}/_{(M)}$ | 0.0045 | 0.009 | 0.018 | .003 |
| Carbon Tetrachloride, gms. | 12.5 | 24.8 | 49.1 | 8.3 |
| Neohexene, gms. | 718.0 | 714.4 | 707.2 | 718 |
| DMAB, gms. | 0.491 | 0.489 | 0.484 | 0.492 |
| Ethylene, ~gms. | 265.6 | 264.2 | 261.5 | 265 |
| | | | | |
| **REACTION CONDITIONS** | | | | |
| Temperature, °C | 90 | 90 | 90 | 90 |
| Pressure, psi | | | | |
| Maximum | 15,000 | 15,000 | 15,000 | 15,000 |
| Final | 12,750 | 12,500 | 12,000 | 13,500 |
| Reaction Time, hours | 3.38 | 4.35 | 4.43 | 4.35 |
| | | | | |
| **PRODUCTIVITY** | | | | |
| Yield, gms. | 62 | 82 | 104 | 58 |
| Conversion, % | | | | |
| On Monomers | 5.03 | 6.1 | ~10.7* | 5.9 |
| On CCl$_4$ | 100 | 90.7 | | |
| Rate, %/hr. (on M) | 1.49 | 1.4 | 2.7 | 1.4 |
| | | | | |
| **PHYSICAL PROPERTIES** | | | | |
| Molecular Weight | 668 | 512 | 373 | 931 |
| Brookfield Vis., cps | 2810 | 1100 | 184 | 22,100 |
| Specific Vis., 80°C | 0.0294 | 0.0209 | .0140 | 0.034 |
| Wt. % Cl | 18.56 | 25.26 | 34.92 | 12.82 |
| Wt. % O | 0.50 | 1.28 | .55 | .48 |
| Functionality (Cl) | 1.748 | 1.824 | 1.84 | 1.68 |
| (O) | 0.104 | 0.205 | .06 | .01 |
| Total | 1.852 | 2.029 | 1.90 | 1.69 |
| Distillate, wt. gms. (50°/55 mm to 125°/2 mm) | 9 | 7 | | |
| Description, Copolymer | Pale, yellow oil ———————————→ | | | white hazy oil |

\* Uncorrected for this run.

FIGURE 1
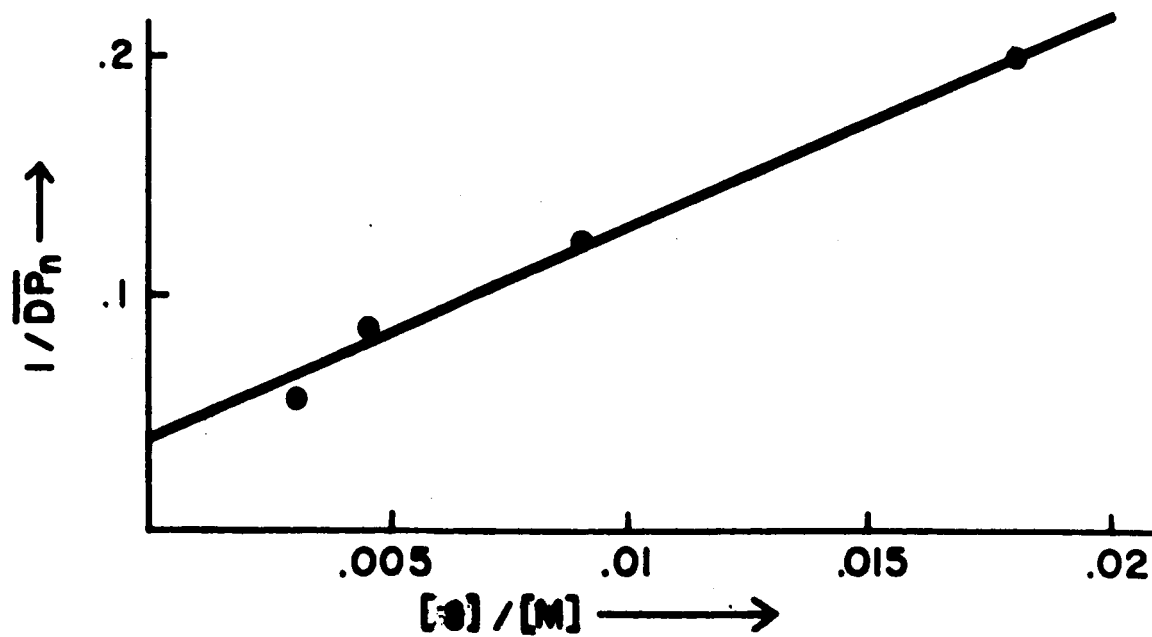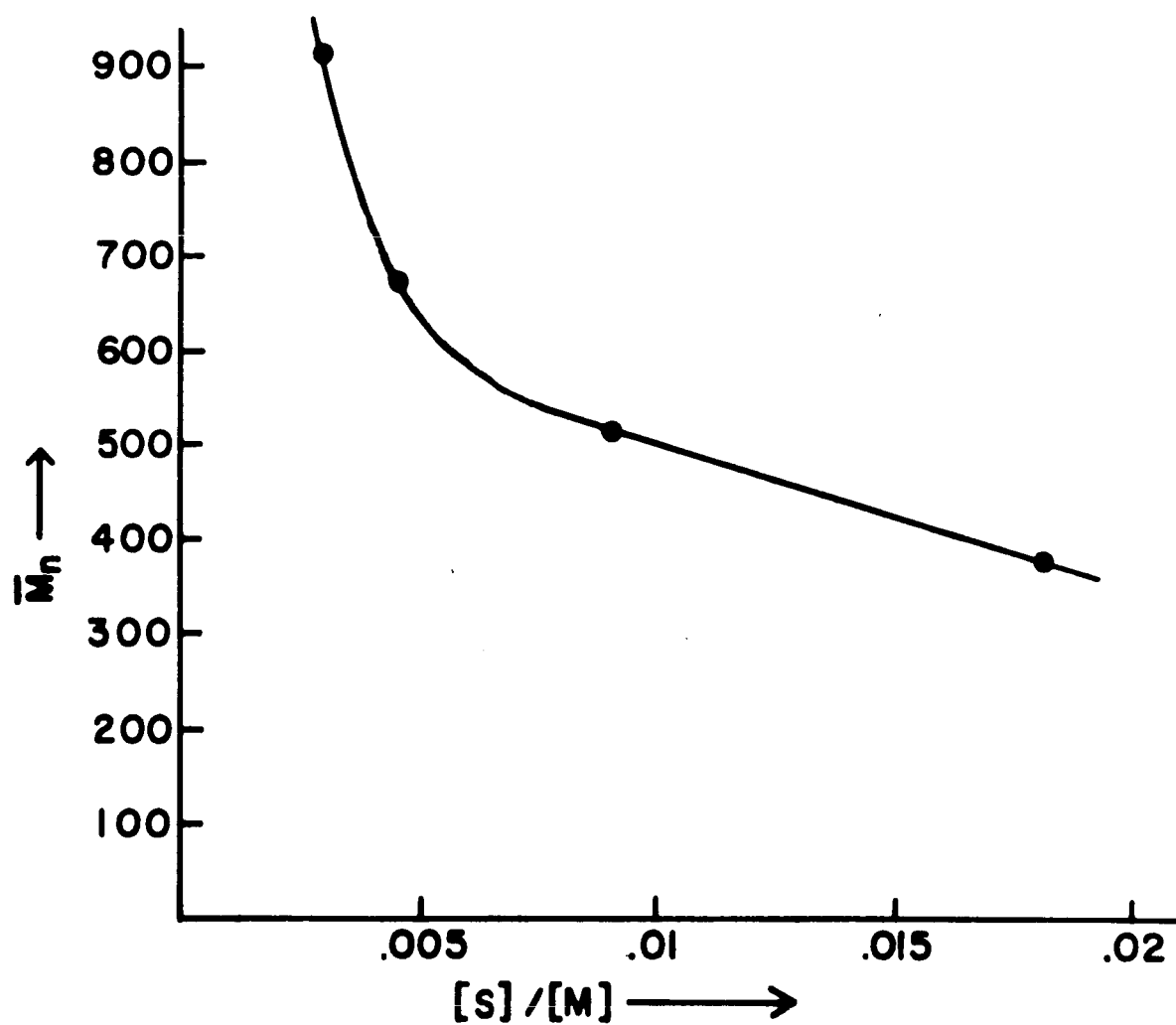
Chemical modification of these telomers is in progress. The goal is conversion of all terminal groups to carboxyl groups. Planned transformations include the following sequence which will result in a dicarboxylic acid when carried out:
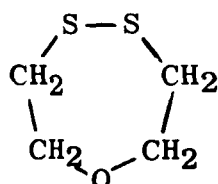
$$Cl - ( \underset{\underset{n}{}}{\overset{\overset{R}{|}}{CH}} - CH_2 )\ CCl_3 \quad \xrightarrow{CN^-}$$

$$N \equiv C - ( \underset{\underset{n}{}}{\overset{\overset{R}{|}}{CH}} - CH_2 )\ CCl_3 \quad \xrightarrow[H_2O]{HNO_3}$$

$$\underset{HO}{\overset{O}{\diagdown}} C - ( \underset{\underset{n}{}}{\overset{\overset{R}{|}}{CH}} - CH_2) - C \underset{OH}{\overset{O}{\diagup}}$$

## D. Disulfides as Telogens

It has been reported that disulfides can serve as active chain transfer agents in free radical polymerizations. Dinaburg and Vansheidt[8] examined a variety of mercaptans and disulfides as chain transfer agents in the polymerization of styrene at 100°C. Simple dialkyl disulfides had chain transfer coefficients from .005 to .01, whereas for some disulfides, such as the dimethyl ester of dithioglycolic acid (I), he reports values as high as 0.1:

$$\underset{CH_3 - O}{\overset{O}{\diagdown}} C - CH_2 - S - S - CH_2 - C \underset{O - CH_3}{\overset{O}{\diagup}}$$

I
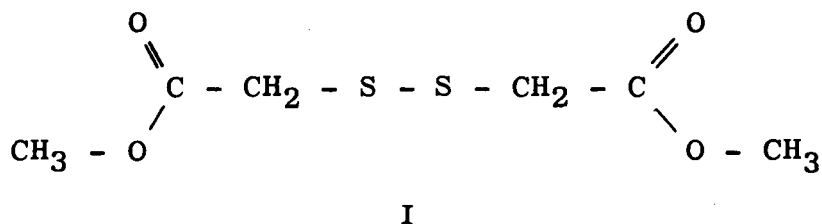
Stockmayer, Howard, and Clarke[9] report that in the polymerization of vinyl acetate, di-n-butyl disulfide has a chain transfer coefficient of 1 and that the diethyl ester of dithioglycolic acid has a coefficient of 1.5. In addition, they reported that the cyclic disulfide 1-oxa-4,5-dithiacyclo-heptane, II, actually copolymerized with the vinyl acetate.

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$$\begin{array}{c} \text{S} - \text{S} \\ \diagup \qquad \diagdown \\ \text{CH}_2 \qquad\quad \text{CH}_2 \\ \diagdown \qquad\qquad \diagup \\ \text{CH}_2 \qquad \text{CH}_2 \\ \diagdown \text{O} \diagup \end{array}$$

<p style="text-align:center">II</p>

A polymer which they prepared had a $\overline{DP}$n of about 90 and had incorporated about 9 disulfide units per molecule. These results were substantiated by Tobolsky and Baysal[10] who were able to copolymerize II with Styrene.

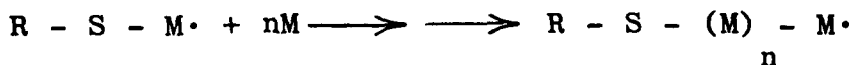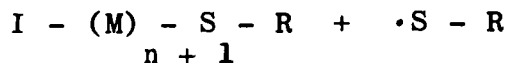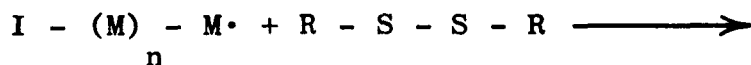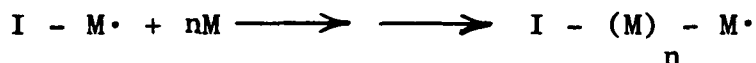The results indicated that the following chain transfer reactions occur when a disulfide is present in a free radical polymerization:

$$I\cdot \;+\; M \;\longrightarrow\; I - M\cdot$$

$$I - M\cdot \;+\; nM \;\longrightarrow\; \longrightarrow\; I - (M)_n - M\cdot$$

$$I - (M)_n - M\cdot \;+\; R - S - S - R \;\longrightarrow$$

$$I - (M)_{n+1} - S - R \;+\; \cdot S - R$$

$$R - S\cdot \;+\; M \;\longrightarrow\; R - S - M\cdot$$

$$R - S - M\cdot \;+\; nM \;\longrightarrow\; \longrightarrow\; R - S - (M)_n - M\cdot$$

$$R - S - (M)_n - M\cdot \;+\; R - S - S - R \;\longrightarrow$$

$$R - S - (M)_{n+1} - S - R \;+\; \cdot S - R$$
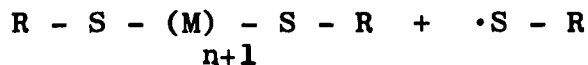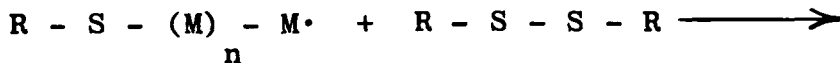
If, as shown above, the disulfide is acyclic, telomers containing two sulfur atoms per molecule result. If the di-sulfide is cyclic, a high polymer containing two sulfide links for every chain transfer step results. In the latter case, the chain transfer reaction is intra-molecular rather than inter-molecular.

In order to apply the disulfide chain transfer reaction to our problem, we prepared several disulfides containing ester functions. We reasoned that if disulfides were effective transfer agents for ethylene–neohexene copolymers, the resulting ester terminal groups could be simply and efficiently converted to the desired carboxyl group. We prepared the following disulfides:
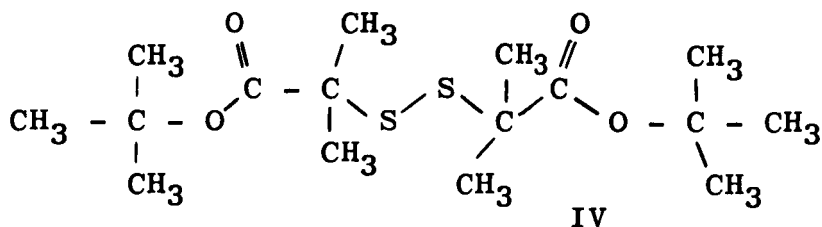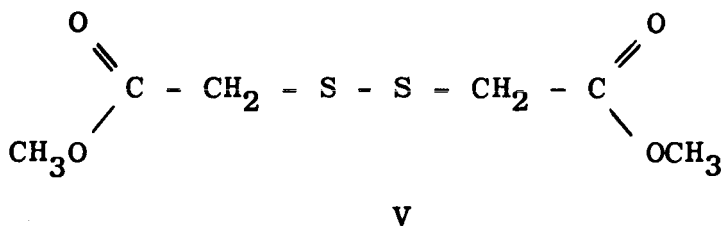
$$CH_3 - O - \overset{\displaystyle O}{C} - CH_2 - CH_2 - CH_2 - S - S - CH_2 - CH_2 - CH_2 - \overset{\displaystyle O}{C} - O - CH_3$$

III

Dimethyl $\gamma, \gamma'$-dithiodibutyrate

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}} - O - \overset{\displaystyle O}{C} - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}} - S - S - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}} - \overset{\displaystyle O}{C} - O - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}} - CH_3$$

IV

Di-t-butyl $\alpha, \alpha'$-dithiobis [isobutyrate]

$$CH_3O - \overset{\displaystyle O}{C} - CH_2 - S - S - CH_2 - \overset{\displaystyle O}{C} - OCH_3$$

V
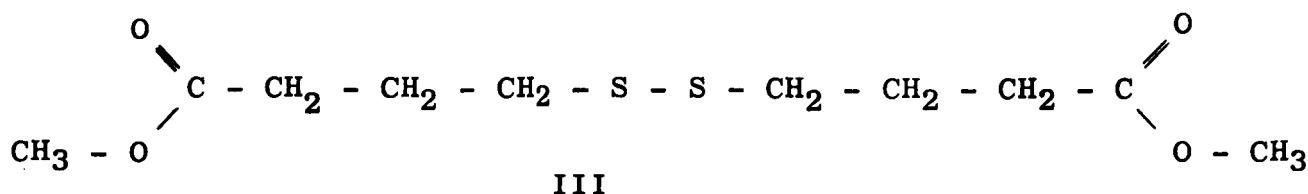
Dimethyl Dithioglycolate

III was prepared by esterifying commercially available dithiodibutyric acid with methanolic HCl. The resulting dimethyl ester boiled at 193°C at 2.0mm. It was a pale straw liquid with a faint peppery odor.

IV was prepared by treating tert-butyl $\alpha$-bromoiso-butyrate with an excess of sodium disulfide. The resulting disulfide boiled at 150-155°C at 2-3mm. It was a colorless oil with a faint garlic odor. tert-Butyl $\alpha$-bromoisobutyrate was on hand as an intermediate in the synthesis of DTAB (See part B, this report).

V was prepared by esterifying commercially available thioglycolic acid with methanolic HCl and oxidizing the resulting mercapto-ester to the disulfide using dimethyl sulfoxide as oxidant:

$$2 \quad \underset{CH_3O}{\overset{O}{\diagdown}} C - CH_2 - SH \quad + \quad CH_3 - \overset{O}{\overset{\|}{S}} - CH_3$$

$$\longrightarrow \quad \underset{CH_3O}{\overset{O}{\diagdown}} C - CH_2 - S - S - CH_2 - C \overset{O}{\underset{OCH_3}{\diagup}}$$

V

$$+ \ H_2O + CH_3 - S - CH_3$$
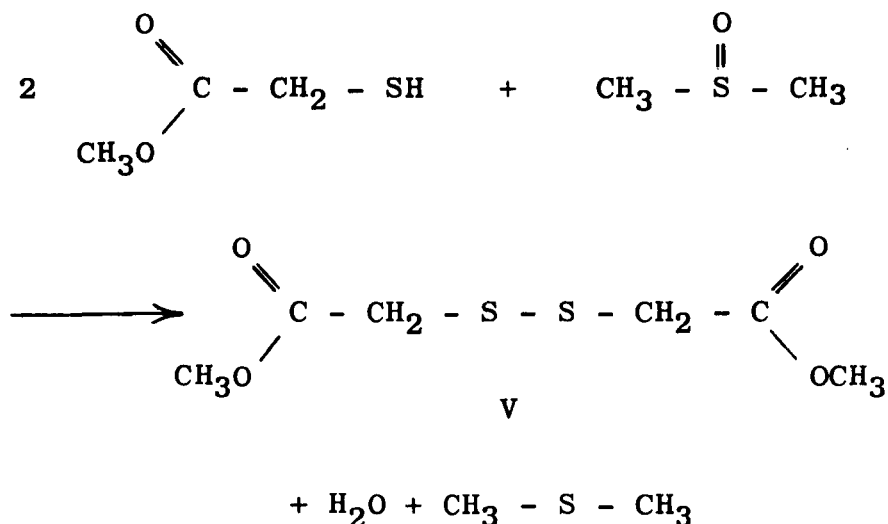
The product boiled at 119-120°C at 1.4mm. It was a pale straw liquid with a strong garlic odor.

As soon as the disulfide telogens were available we started telomerization studies in the 1.5 $\underline{l}$ stirred autoclave. The results of these experiments are summarized in table III.

The low polymerization rate for the runs shown in table III is partly due to the low initiator (DMAB or DTBP) concentration used, but may also reflect a low efficiency of disulfides III and IV as telogens, i.e., they may act as retarders. This would be the case if the reaction between a radical and the disulfide (to produce a sulfide terminated chain and a sulfide radical) were rapid, but initiation of a subsequent polymer chain by the resulting sulfide radical were slow.

Preliminary analytical data indicate that the functionalities obtained in these runs were low. This will be discussed in a later report when the analyses are complete.

Telomerization studies will continue using disulfide telogen V.

- 14 -

## TABLE III

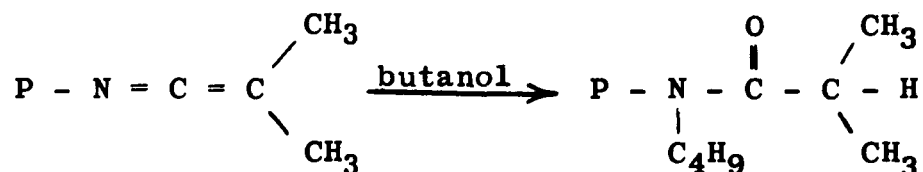### NEOHEXENE/ETHYLENE COPOLYMERS PREPARED IN THE STIRRED AUTOCLAVE

| Run No. 23EMS | 88 | 91 | 92 | 89 | 94 | 101 | 105 | 106 |
|---|---|---|---|---|---|---|---|---|
| **Initial Charge** | | | | | | | | |
| Disulfide Telogen | III | III | III | IV | IV | IV | III | IV |
| Disulfide wt., gms | 5.0 | 5.0 | 9.62 | 5.0 | 12.66 | 12.66 | 10.00 | 10.00 |
| Neohexene, gms. | 720 | 720 | 720 | 720 | 720 | 720 | 687.7 | 687.7 |
| DMAB Cat., gms. | 0.491 | 0.491 | 0.491 | 0.491 | 0.491 | 0.491 | 0.491 (DTBP).1 | 0.491 (DTBP).1 |
| Ethylene, gms. | 265 | 265 | 262 | 265 | 262 | 262 | 254.3 | 254.3 |
| Mol Ratio, Telogen/Monomers | 0.001 | 0.001 | 0.002 | 0.0008 | 0.002 | 0.002 | .002 | .0016 |
| **Reaction Conditions** | | | | | | | | |
| Temperature, °C. | 90 | 90 | 90 | 90 | 90 | 90 | 160 | 160 |
| Pressure, psig. | | | | | | | | |
| Initial (@ R.T.) | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 | - | - |
| Maximum | 15,000 | 15,000 | 15,000 | 15,000 | 15,000 | 15,000 | 15,000 | 15,000 |
| Drop | 1000 | 1500 | 3000 | 1250 | 1750 | 1000 | 2900 | 2250 |
| Reaction Time, hrs. | 4.35 | 4.35 | 4.35 | 4.35 | 4.35 | 2.17 | 3.3 | 3.3 |
| **Productivity** | | | | | | | | |
| Yield, gms. | 30 | 37 | 37 | 35 | 46 | 31 | 60 | 37 |
| Conversion, % | 3.05 | 3.76 | 3.77 | 3.55 | 4.68 | 3.16 | 6.4 | 4.0 |
| Rate, %/hr. | 0.70 | 0.86 | 0.87 | 0.82 | 1.08 | 1.46 | 2.0 | 1.2 |
| Product Description | Colorless Very hazy Very viscous Oil | | Colorless Clear Viscous Oil | | 51. yellow Clear Oil | | Very Hazy Yellow Oil | Deep yellow Clear Oil |

DMAB = Dimethyl 2,2'-Azobisisobutyrate

DTBP = Di tert -Butyl Peroxide

## E. Residual Non-COOH Functionality in Hydrolyzed Products Derived from AIBN

In part B of the technical discussion of our third quarterly report, we reported the analytical data obtained upon some molecular distillation fractions derived from a hydrolyzed copolymer prepared with AIBN initiator. In that disucssion we interpreted the data to indicate the presence of oxygen-containing functional groups other than carboxyl. The low nitrogen level remaining in these samples (between 1/4 and 1/2 nitrogen per molecule) suggested that at least part of the oxygen could be present in an amide structure derived from a ketene-imine end group by solvolysis:

$$
P - N = C = C \begin{array}{c} \diagup CH_3 \\ \diagdown CH_3 \end{array} \xrightarrow{\text{butanol}} P - \underset{\underset{C_4H_9}{|}}{\overset{\overset{O}{\|}}{N}} - C - C \begin{array}{c} \diagup CH_3 \\ -H \\ \diagdown CH_3 \end{array}
$$

P = polymer chain.

However more excess oxygen was present than could be accounted for by this explanation.

Table IV summarizes the earlier results and shows that there are about twice as many excess oxygen atoms per molecule as there are residual nitrogen atoms per molecule. The "composite sample" is simply a weighted average of the properties of the five distillation fractions and the residue. If all the nitrogen in this sample is present as amide, it contains only the average $\sim.8$ COOH groups, $\sim.4$ amide groups and $\sim.3$ other oxygen functions (probably hydroxyl) per molecule. This adds up to a total of 1.5 functional groups per molecule for the whole hydrolyzed product. Fractions 5 and the residue are even higher in total functionality: both have 1.9 groups per molecule.

One must be quite cautious about taking this type of functionality determination too literally, because the quantities involved, especially the nitrogen analyses, are quite small. The usual accuracy quoted for a nitrogen determination is $+ .3\%$. Note that the nitrogen reported in these samples was between .27 for fraction 1 and .50 for fraction 5.

We have also analyzed some of the hydrolyzed AIBN products for double bond content using the Wijs Iodine

| | CN Term. Precursor | Distillation Fractions | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample | | 1 | 2 | 3 | 4 | 5 | R | Comp. |
| gms. obtained | 1209 | 289 | 147 | 157 | 103 | 38 | 336 | 1070 |
| Wt. % O | .88 | 12.57 | 12.14 | 11.00 | 9.97 | 8.73 | 6.28 | 9.92 |
| Wt. % N | 6.75 | 1.61 | 1.65 | 1.68 | 1.42 | 1.34 | .86 | 1.35 |
| $\overline{M}n$ (THF) | 385 | 234 | 296 | 380 | 436 | 518 | 802 | 372 |
| Neut. Eq. | - | 410 | 360 | 358 | 431 | 567 | 645 | 450 |
| Nit. Eq. Wt. | 207 | 872 | 850 | 835 | 988 | 1048 | 1630 | 1039 |
| Ox. Eq. Wt. | 1820 | 127 | 132 | 145 | 160 | 183 | 255 | 161 |
| CN Eq. Wt. | ~420 | - | - | - | - | - | - | - |
| COOH/mol. | - | .57 | .82 | 1.06 | 1.01 | .92 | 1.24 | .83 |
| N/mol. | 1.86 | .27 | .35 | .45 | .44 | .50 | .49 | .36 |
| O/mol. | .21 | 1.84 | 2.24 | 2.62 | 2.73 | 2.84 | 3.14 | 2.31 |
| non-COOH O/mol. | .21 | .70 | .60 | .50 | .71 | 1.00 | .66 | .65 |
| CN/mol. | ~.9 | - | - | - | - | - | - | - |
| Total* | - | 1.3 | 1.4 | 1.6 | 1.7 | 1.9 | 1.9 | 1.5 |

TABLE IV

TOTAL FUNCTIONALITIES OF AIBN PRODUCTS

\* See text for explanation

monochloride titration method.  For example, hydrolyzed 22-EMS-50 had a C=C equivalent weight of 1600, corresponding to about .23 C=C per molecule.

## VI.  PLANS FOR FUTURE WORK

In the next quarter we plan to continue our disulfide telomerization studies using the dimethyl ester of dithioglycolic acid as telogen, and we will finish the evaluation of the products prepared with the other disulfide telogens.

We will also continue our efforts to convert the chloride and trichloromethyl end groups of the $CCl_4$ telomers to useful functional groups.

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